Methane turnover in exposed sediments of an Amazon floodplain lake

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Abstract. In the Amazon floodplain large areas of unvegetated lake sediments are exposed to air during low water. I measured methane fluxes from exposed sediments of an Amazonian floodplain lake and assessed the regulating factors. Methane emission decreased from values between 10 and 40 μmol CH_4 m^{-2} h^{-1} to zero when the sediments were exposed to air. Mean fluxes were about 3.7 μmol CH_4 m^{-2} h^{-1}. Fluxes were low compared to measurements taken from flooded habitats making exposed lake sediments a negligible source of atmospheric CH_4. This was mainly due to the lack of ebullition which governs methane flux in the flooded phase. Methane oxidation at the sediment surface consumed up to 75% of the methane entering the oxidised zone. Compared with CO_2 emission methane turnover was of minor importance for the carbon budget of the sediments.

Introduction

Wetlands are an important source of atmospheric methane contributing about 20% to the global methane source strength (Houghton et al. 1995). The seasonally flooded floodplain of the Amazon basin is one of the largest wetlands on earth and contributes significantly to global methane emission (Bartlett et al. 1988; Crill et al. 1988; Devol et al. 1988). The Amazon floodplain consists of three habitats: open water, floating vegetation and seasonally flooded forests (Junk 1997). Methane emissions from these habitats ranged from 31 to 229 μmol CH_4 m^{-2} h^{-1} for open waters (Devol et al. 1988; Devol et al. 1990), 91 to 1536 μmol CH_4 m^{-2} h^{-1} for floating vegetation (Wassmann & Thein 1996; Devol et al. 1988) and 18 to 599 μmol CH_4 m^{-2} h^{-1} for flooded forest (Devol et al. 1990; Bartlett et al. 1990). These emissions from the Amazon floodplain are estimated to contribute about 1–8% to the global methane emission from wetlands (Wassmann & Martius 1997). However, previous studies focused solely on emissions during the flooding period. Normally less than 25% of the Amazone floodplain are

covered by permanent lakes (Crill et al. 1988; Wassmann & Martius 1997) and the remaining area of the floodplain is subject to alternating flooded and dry conditions. Depending on topography and hydrology, the period during which the area is exposed to air can be less than a month to almost the entire year. Emission data from the non-flooded soils are scarce. The only study conducted with moist (but non-flooded) soils reports fluxes between -31 and 378 μmol CH_4 m^{-2} h^{-1} (Devol et al. 1988).

During the phase of lowest water level large areas of unvegetated lake sediments of the Amazon floodplain are exposed to air. These semiaquatic sediments represent a distinct type of habitat which is associated with high emissions of nitrous oxide during the terrestrial phase (Kern et al. 1996). One goal of my study was to quantify the methane source strength of exposed semiaquatic sediments in order to make a more accurate estimate of the Amazones methane budget.

To predict the effects of land use and/or climate changes on the methane flux and to apply the results of flux measurements to other regions one has to understand the underlying regulatory mechanisms. Methane emission is expected to decrease when the soil dries. This might be due to inhibition of methanogenic bacteria by oxidised conditions or due to increased microbial methane oxidation (Henckel & Conrad 1998). We measured fluxes as well as methane production in order to find out what role the two mechanisms play in regulating the methane flux in lake sediments which are exposed to the atmosphere.

Material and methods

The study was carried out on Marchantaria Island ($3°13.947'$ S and $59°56.765'$ W; 21.6 m above sea level), an island in the Amazon river near Manaus, Brazil. Seasonal water level fluctuations of about 10 m lead to predictable annual inundation of the floodplain. A detailed description and an overview of former research on the island has recently been published (Junk 1997). The study site is a shallow part of lake Camaleão which dries out for about three months between October and January (21.6 m above sea level). The sediment was a silt loam (8/55/37% clay/silt/sand), the pH (water) was 6.3, total carbon content was 1.16% (Table 1).

The sediment was free of macrophytes. In 1996, the site dried on October 18th, in 1997, on October 20th. Measurements were carried out *in situ* at different times after the sediment dried.

In 1996 **methane fluxes** were measured using small glass domes (Kern et al. 1996; modified from Stal 1988). Seven such domes were inserted into the sediment creating a headspace of 20 ml (area 15.9 cm^2). After one hour, three

Table 1. Characteristics of flooded and not-flooded sediment.

	Flooded	Exposed to air
pH (water)	7.3[1]	6.3[4]
Bulk density [g cm^{-3}]	0.93 ± 0.05[2]	1.64 ± 0.11[4]
Total carbon [%]	1.13 ± 0.06[3]	1.16 ± 0.03[4]
Respiration [mol CO_2 m^{-2} h^{-1}]	nd	3 ± 1.75 [4]

[1] 13.8.1996, [4] 27.11.1996, [3] 23.4.1997, [2] 20.3.1997, nd: not determined.

of the glass domes were sampled using 7-ml vacutainers (Becton Dickinson, Plymouth, U.K.). After three hours the remaining headspaces were sampled. 250 μl gas samples from the vacutainers were analysed during the following days. Because we took a large sample from a small headspace, the pressure in the vacutainers was below atmospheric pressure. To correct for this we took subsamples from the vacutainers using a pressure lock syringe, compressed the gas sample in the syringe to 250 μl and then allowed pressure equilibration by submerging the needle in distilled water and opening the pressure lock vent until no more gas bubbles escaped. The vent was then closed and the sample was injected into a gas chromatograph equipped with a flame ionisation detector (Kern et al. 1996).

The CH_4 flux was calculated from the difference in the CH_4 content of the vacutainers sampled after 3 hours and the mean CH_4 content after 1 hour.

Methane production was determined in the same way by using glass domes with acetylene added. Eight glass domes were inserted into the sediment. After capping, acetylene was added to the headspaces to a final concentration of 10%. A pressure equilibration was achieved with a small needle which was withdrawn after the acetylene addition. The methane fluxes were determined as described above. It was assumed that acetylene inhibited methane oxidation as well as production, but that inhibition of methane production did not result in short term changes of the methane flux (King 1996). Thus the acetylene treated flux represents the total methane production while the difference between production and actual flux represents the rate of methane oxidation. Small glass domes as static chambers has allready been used to study nitrogen fixation (Stal 1988) and denitrification (Kern et al. 1996). This technique was chosen because it is possible to measure denitrification, nitrogen fixation, trace gas fluxes and methane oxidation in one and the same experiment (manuscript about the nitrogen data in preparation).

To check this technique for sampling errors and nonlinearity of the methane flux, in **1997 the methane flux** was measured using static chambers made of polyethylene (inner diameter 17 cm, height 10 cm). The boxes were

driven 2 cm into the sediment and then closed. Pressure equilibration was achieved by means of a small rubber tubing connected to the lid. Gas samples (3 ml) were taken every 10 min over a period of 40 min from a silicone septum and transferred to 3 ml vacutainers which were previously filled with distilled water. In each vacutainer the water was replaced by injecting the gas sample into the vacutainer while water escaped through another needle. The CH_4 flux was calculated from the linear change of the CH_4 mixing ratio inside the chamber. Values are mean and standard deviation of three replicate chambers. Parallel measurements with glass domes and polyethylene chambers proved that both techniques gave the same results (data not shown). Methane production was measured the same way as in 1996; using seven replicates each after one and three hour intervals.

The **methane concentration in porewater** from different sediment layers was determined by sampling three replicate sediment cores with a cut syringe (inner diameter 12 mm), rapidly transferring 1 cm or 2 cm slices of the sediment into small glass bottles (10.8 ml) containing 1 ml distilled water and sealing the bottles with black rubber stoppers. After manual shaking of the small glass bottles for five minutes, 3 ml gas samples from the headspaces were transferred to 3 ml vacutainers. Bottles containing only 1 ml of water but no sediment were sampled as a control. The water content of the sediment was determined gravimetically and the porewater concentration of methane was calculated using a Bunsen solubility coefficient of 0.029 at 30 °C (L'air liquide 1976).

From the vertical profiles of methane in the sediment, diffusive fluxes were calculated by applying Fick's first law:

$$J_D = -\Phi D_s(dC/dz)F.$$

where J_D = diffusive flux (μmol CH_4 m^{-2} h^{-1}), Φ porosity of the sediment (0.51–0.62 ml ml^{-1}), D_s = sediment diffusion coefficient (cm^2 s^{-1}), dC/dz = the measured CH_4 concentration gradient (μmol l^{-1} cm^{-1}) and F = unit conversation factor (36000 l cm^{-1} m^{-2} s h^{-1}). The bulk sediment diffusion coefficient D_s was calculated from the molecular diffusion coefficient (D = 1.95 × 10^{-5} cm^2 s^{-1}) by correction for porosity and tortuosity using the empirical equation $D_s = D \Phi^2$ (Lerman 1988).

Integration of flux data was carried out with the graphical software ORIGIN 5.0 (Microcal, Inc., Northhampton, MA).

Vertical profiles of the redox potential were measured in the field using a platinum electrode. A small piece of platinum wire (diameter 0.05 mm) was melted in the tip of a fine drawn capillary. The silver/silver chloride electrode of a pH electrode was used as reference and a portable pH meter as voltmeter. The electrode was checked with a standard redox solution (Deutsche

Einheitsverfahren 1984). It was inserted into the sediment by means of a micromanipulator. The micromanipulator was fixed to a piece of wood which was driven into the sediment. The signal was assumed constant when the drift was slower than 1 mV min^{-1}. Typical equilibration times were between 2 and 30 minutes. To refer the results to a standard hydrogen electrode the potential of the reference electrode (203 mV at 30°; from Deutsche Einheitsverfahren 1984) was added.

Soil respiration measurements were carried out by means of a portable soil respiration measuring system developed by PP-Systems, Hitchin, U.K. This system is based on the EGM-1 environmental gas monitor and a dynamic SCR-1 soil respiration chamber. CO_2-zero setting was done with normal air. Total carbon was determined in dried sediment samples using a CN analyser (Carlo Erba Intruments NA1500).

Results

Methane flux rates were generally high during the initial phase of the dry period. After a short period of high fluxes the methane fluxes decreased to values not significantly different from zero. In 1996, the period of high fluxes (up to 40 μmol CH_4 m^{-2} h^{-1}) lasted only 3 days. After one week, fluxes were $<$5 μmol CH_4 m^{-2} h^{-1} (Figure 1). In 1997, the period of high activity lasted for at least 2 weeks, but maximum fluxes were lower than in 1996 (Figure 2). Total integrated methane emission during the periods investigated were about 3.75 mmol m^{-2} in both years, which corresponds to a mean rate of 3.33 μmol CH_4 m^{-2} h^{-1} in 1996 and 4.11 μmol CH_4 m^{-2} h^{-1} in 1997. In 1996 negative fluxes occurred after one month of sediment exposure. Fluxes were -2.24 ± 1.32 and -2.92 ± 1.17 μmol CH_4 m^{-2} h^{-1} on November 20th and 27th respectively.

Methane production exceeded the methane flux with one exception. On 10/18/96, 10/20/97 and when fluxes were around zero, production and flux were not significantly different from each other. Total methane production during the period investigated was 9.87 mmol m^{-2} in 1996 and 12.47 mmol m^{-2} in 1997 respectively. This means that 62% and 72% of the methane produced was oxidised in the oxic sediment surface before it could enter the atmosphere. The high standard deviation of the measurements prevents a more detailed interpretation of the data. However, as a trend, the ratio of methane production to methane flux was rather constant, and thus the absolute extent of methane oxidation decreased with time. This means that the decrease of the methane emission during the exposed period was primarily caused by the decrease in methane production.
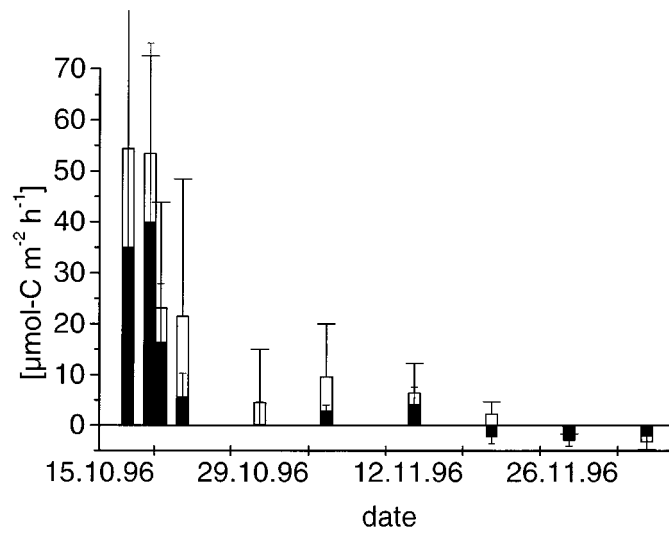
Figure 1. Methane flux (black columns) and production (white columns) in exposed sediments during the exposed period 1996.
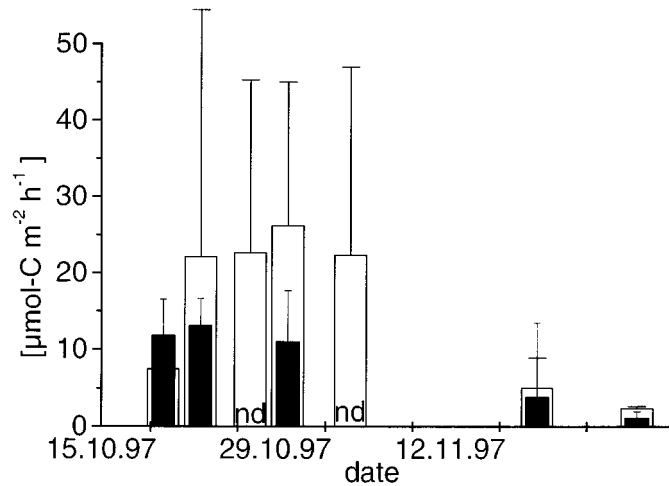

Figure 2. Methane flux (black columns) and production (white columns) in exposed sediments during the exposed period 1997. nd = flux not measured.

After one week of the drying period methane increased linearly with depth (Figure 3). The porewater methane concentration reached saturation at 8 cm depth on 27 October 1997. Although gas bubbles occurred in the sediment, ebullition was never observed. Two weeks later, the methane concentration in the sediment was much lower and the highest concentration was found at 4 cm depth. However, methane concentration at 4 cm depth was not significantly
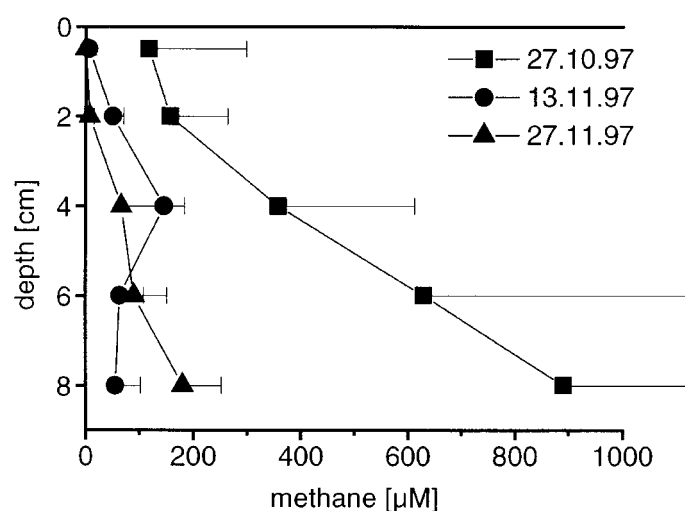
Figure 3. Vertical profiles of methane concentration in the porewater at 3 different days. Values are mean and standard deviation of 3 independent profiles.

different from concentrations below this depth. One month after exposure of the sediments, methane increased gradually with depth indicating a source below 8 cm. Diffusive fluxes of methane out of the sediment were calculated from the depth profile at the surface. The highest vertical flux was calculated from the steepest part of the gradient found in the sediment (Table 2). The values compared fairly well with directly measured values except on 27.10.97 when the calculated fluxes were lower than the measured ones. However, on this occasion one of the three samples from 1 cm depth contained an especially high methane concentration creating a large standard deviation. Removal of this data leads to a calculated surface flux of 13.14 μmol CH_4 m^{-2} h^{-1}. From the porewater profiles it could be calculated that 19.21 mmol CH_4 m^{-2} were removed from the upper 9 cm of the sediment column between October 27th and November 27th. The integrated flux data of 3.75 mmol CH_4 m^{-2} can explain only 20% of this methane loss. The rest must have been oxidised in the sediment.

The redox potential at the sediment surface was always positive and increased from 100 mV to 400 mV during the period investigated (Figure 4). Eh was highest between 0.5 an 1 cm depth. Below 1 cm depth the redox potential dropped to negative values. Sediment respiration was 6917 ± 1167 μmol CO_2 m^{-2} h^{-1} on 13.11.96 ($n = 5$) and 3000 ± 1750 μmol CO_2 m^{-2} h^{-1} on 27.11.96 ($n = 4$) which is at the lower end of values reported for tropical soils (Raich & Schlesinger 1992). Even considering maximum methane emission, the CO_2 flux exceeded the CH_4 flux by a factor of more than 75 and

Table 2. Methane flux at the sediment surface and in the zone of highest flux calculated from depth profiles (Figure 3) and directly measured flux and production.

	27.10.97	13.11.97	27.11.97
Calculated from profiles			
Surface flux [μmol CH_4 m^{-2} h^{-1}]	3.6	5.05	0.66
Highest flux [μmol CH_4 m^{-2} h^{-1}]	12.31	6.54	2.57
% oxidised	71	23	74
Directly measured			
Surface flux [μmol CH_4 m^{-2} h^{-1}]	11 ± 6.7[1]	3.8 ± 9.6[2]	1.14 ± 0.79
Production [μmol CH_4 m^{-2} h^{-1}]	22.6 ± 22.6	5 ± 3.9[2]	2.33 ± 0.26
% oxidised	51 ± 83	24 ± 145	51 ± 23

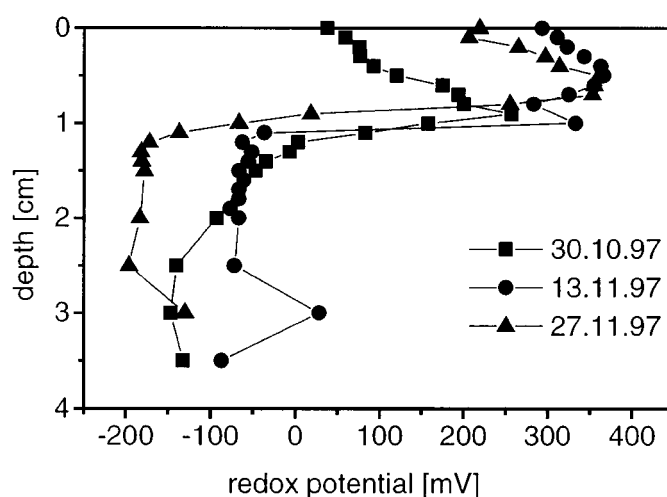[1] measured 30.10.1997; [2] measured 19.11.97

Figure 4. Vertical profiles of the redox potential measured *in situ*.

therefore methane emission was of minor importance for the carbon budget of the sediments during the exposed period.

Discussion

During the 3 months of lowest water, 0.9 km^2, which is 14% of the overall area of Lake Camaleão dries out (Kern & Darwich 1997). Assuming that the Lake Camaleão area is typical of the Amazon floodplain, on an annual base semiaquatic sediments represent 3.5% of the entire floodplain (ca. 180000

km^2, Wassmann & Martius 1997). If we consider only the period investigated and assume fluxes after about one month of exposure to be negligible, semi-aquatic sediments emit 0.06 g CH_4 m^{-2} yr^{-1}. This adds 0.0004 Tg CH_4 yr^{-1} to the current estimate of the global source strength of the Amazon flood-plain being 1–9 Tg CH_4 yr^{-1} (Wassmann & Martius 1997). Thus, exposed semiaquatic sediments do not significantly contribute to methane emission from the Amazon floodplain. The main effect of drying lake sediments on the methane budget of the ecosystem is the reduction of the otherwise high methane emission during the flooded phase.

My flux measurements are subject to a high standard deviation. Since I used rather small chambers this variability might reflect the spatial hetero-geneity of the rather uniform looking sediment. However, the results obtained by direct flux measurements and calculations from the vertical gradient of methane in the sediment agreed fairly well, demonstrating the applicability of both methods. In sediment water systems, calculation of fluxes from pore-water concentrations is a common technique (Crill et al. 1988; Frenzel et al. 1990). In water saturated soils sampling of vertical profiles of methane might be a useful complement to direct flux measurements. Flux measurements can be verified; and the shape of the gradient gives information about the location of net activities in the sediment. However, flux determinations from gradients are very sensitive to changes in the measured gradient and to estimates of the diffusion coefficient D_s. In future studies, the spatial resolution of the surface gradient should be improved (King 1996). The effective diffusion coefficient is commonly estimated from porosity data by using empiric equa-tions (Lerman 1988) and the obtained values are comparable to measured diffusion coefficients (Van Rees et al. 1991). However, the precision of the determination of diffusion coefficients depends on the sediment structure, and might be too imprecise in more stratified or heterogeneous sediments.

The vertical profiles of the redox potential demonstrate that methanogen-esis below the oxidised surface layer was possible even after one month of exposure. Usually, methane production in soils occurs at redox potentials below -150 mV (Jugsujinda & Patrick Jr. 1996). I observed a subsurface maximum of the redox potential at a depth of one centimeter and for this I can offer no adequate explanation. Probably an insufficient contact of the elec-trode tip with the soil solution in the not fully saturated uppermost millimetres led to incorrect low Eh values at the sediment surface. In spite of the high vari-ability and errors related to redox measurements in sediments, Eh is a usefull qualitative marker to detect reducing conditions in the sediment (Patrick et al. 1996). The redox profiles shown in Figure 4 demonstrate that below 1 cm the sediment remained reduced throughout the entire period. Oxidation of deeper layers was prevented because the bulk sediment remained water saturated

throughout the entire observation period (data not shown). Methane oxidation was only possible in the uppermost centimetre of the sediment. Total carbon content of the sediment was rather homogenous in the top 10 centimetres (data not shown, see also Kern 1995) which means that organic substrates for methanogenesis were available even in deeper sediment layers. The lack of stratification can be explained by the recent nature of the sediment. In the area I studied, I observed an annual sedimentation rate of several centimetres.

The vertical profiles of methane in porewater show that the deeper sediment layers remained a source of methane throughout the exposed period. The concave shaped profile at the surface demonstrates methane consumption in the upper sediment layer (Frenzel et al. 1990). High concentrations of porewater methane were also found in a flooded sediment of an Amazonian floodplain lake (Crill et al. 1988). I did not measure methanogenesis directly but determined the highest vertical flux of methane within the sediment. From the data it is not possible to say if methanogenesis took place during the period of investigation, or if the deeper sediment was just losing methane during the exposed period. The total amount of methane lost from the upper 8 cm of the sediment between 27 October and 27 November was about 5 times higher than the integrated flux during the same period. Thus, the methane storage in the sediment was high enough to drive the measured flux during the exposed period.

Since methane oxidation consumed less than 75% of the methane diffusing upward but the measured fluxes were a factor 100 lower than reported for open water (Wassmann & Thein 1997) I conclude that the difference to the flooded state was not caused by increased methane oxidation in the oxic surface layer. The predominant pathway for vertical methane transport in flooded areas of the Amazon floodplain is ebullition which contributes 73–85% to the overall methane emission (Crill et al. 1988; Devol et al. 1988; Wassmann et al. 1992). During the dry period ebullition was prevented by compaction of the sediment. The bulk density of the 1–10 cm layer doubled from 0.9 g cm^{-3} in the flooded season to 1.8 g cm^{-3} in the exposed season (Table 1). I never observed ebullition during my flux measurements, while in still flooded parts of the lake nearby, ebullition was observed with high frequency.

Summarising these results, I propose a two-step mechanism for the reduction of the methane flux from exposed lake sediments. In the first step, the flux is greatly reduced because ebullition is blocked when the sediment dries. In a second step the methane flux out of the reduced zone decreases gradually during the dry phase.

Acknowledgements

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